

REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports (0704-014302). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not have a valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

AFRL-SR-AR-TR-03-

0458

1. REPORT DATE (DD-MM-YYYY) 10-15-2003		2. REPORT TYPE Final Technical Report		01 May 2000 – 30 April 2003	
4. TITLE AND SUBTITLE Development of Nonlinear Optical Materials (LBO, BBO, and KTP) for Use in High-Power Lasers				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER F49620-00-1-0301	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Halliburton, Larry E. Giles, Nancy C.				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) West Virginia University Research Corp. Office of Sponsored Programs 886 Chestnut Ridge Road PO Box 6845, Morgantown, WV 26506				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Office of Scientific Research 801 N. Randolph St. Room 732 Arlington, VA 22203-1977				10. SPONSOR/MONITOR'S ACRONYM(S) AFOSR/NE	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT Distribution unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT This is the final technical report for a three-year project to identify and characterize point defects in single crystals of LiB ₃ O ₅ (LBO), β-BaB ₂ O ₄ (BBO), KTiOPO ₄ (KTP), KH ₂ PO ₄ , and ZnO. These materials are used to generate ultraviolet laser beams, and their performance is often limited by the presence of optically active point defects. In this project, we have investigated a variety of electron and hole traps and have shown how they affect the behavior of devices. The experimental techniques used to characterize the crystals were optical absorption, visible photoluminescence, electron paramagnetic resonance (EPR), photoinduced EPR, and electron-nuclear double resonance (ENDOR). Industrial collaborators included Northrop Grumman (formerly Litton Airtron Synoptics), Lightwave Electronics, Crystal Associates, Cleveland Crystals, and Cristal Laser. Specific results during this project include (1) a detailed characterization of Ti ³⁺ centers in KTP, (2) identification of self-trapped hole centers in LBO and BBO crystals, (3) identification of oxygen vacancies as the primary electron trap in LBO, BBO, and KH ₂ PO ₄ crystals, (4) production of neutral isolated nitrogen acceptors in ZnO crystals, and (5) observation of Ag ⁰ atoms and Ag ²⁺ ions after diffusion of silver into BBO crystals.					
15. SUBJECT TERMS nonlinear optical materials, harmonic generation, high-power ultraviolet lasers, point defects, optical absorption, electron paramagnetic resonance, electron nuclear double resonance, photoluminescence, LiB ₃ O ₅ , β-BaB ₂ O ₄ , KTiOPO ₄ , KH ₂ PO ₄ , ZnO					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES 12	19a. NAME OF RESPONSIBLE PERSON Larry E. Halliburton
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER 304-293-3422, ext. 1442

20031120 004

DISTRIBUTION STATEMENT A
Approved for Public Release
Distribution Unlimited

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

FINAL TECHNICAL REPORT
(For project period from May 1, 2000 to April 30, 2003)

TABLE OF CONTENTS

	page
I. Project Overview.....	2
II. Students, Publications, and Presentations.....	3
III. Highlights of Research Results.....	5
A. Minimizing Laser-Induced Gray Tracks in KTP Crystals.....	5
B. Identification of Electron and Hole Traps in KDP Crystals.....	6
C. Production of Nitrogen Acceptors in ZnO.....	6
D. Role of Copper in the Green Luminescence from ZnO.....	7
E. EPR and ENDOR from Ti^{3+} Centers in KTP Crystals.....	8
F. EPR and ENDOR Study of Trapped Hole Centers in LBO.....	9
G. EPR Study of Electron and Hole Traps in BBO Crystals.....	10
H. Diffusion of Silver into BBO Crystals.....	10
I. Origin of Ultraviolet Absorption in LBO Crystals.....	11
J. Room-Temperature-Stable Point Defects in BBO Crystals.....	12

I. Project Overview

This document is the final technical report for work performed under Air Force Office of Scientific Research (AFOSR) Grant F49620-99-1-0301. The report covers the entire three-year period of the project. The title of the project is "Development of Nonlinear Optical Materials (LBO, BBO, and KTP) for Use in High-Power Lasers" and the Principal Investigators are Larry E. Halliburton and Nancy C. Giles, Physics Department, West Virginia University. In this three-year research program, which started May 1, 2000, studies were conducted to identify and characterize device-limiting point defects in single-crystals of LiB_3O_5 (LBO), β - BaB_2O_4 (BBO), and $KTiOPO_4$ (KTP). These materials are widely used to generate high-power visible and ultraviolet laser beams by harmonic generation. In this process, longer-wavelength lasers in the near infrared are converted to the shorter wavelengths. These crystals have large nonlinear coefficients and sufficient birefringence for phase matching. The Air Force and the MDA have significant interest in developing these materials for use in future directed energy weapons systems.

The primary focus of this project was to use spectroscopic techniques to investigate the variety of point defects found in the LBO, BBO, and KTP crystals. At the request of the AFOSR program manager, we extended the project to include KH_2PO_4 (KDP) and ZnO. Electron paramagnetic resonance (EPR), electron-nuclear double resonance (ENDOR), optical absorption,

and photoluminescence were among the experimental techniques used. Scientists at the Air Force Research Laboratory (Wright-Patterson AFB in Dayton, OH) were co-authors on two papers. These were Dr. Nils Fernelius and Dr. David Look. Industrial participants in this research include Northrop Grumman (formerly Litton Airtron Synoptics), Lightwave Electronics, Cleveland Crystals, Coherent Crystal Associates, and Cristal Laser. Additional collaborators were located at Stanford University, Lawrence Livermore National Laboratory, and Hebrew University in Jerusalem. As a result of this project, three students have been received their PhD degree in materials physics, ten refereed papers have been published in the scientific literature, and four presentations have been made at national and international conferences.

II. Students, Publications, and Presentations

Graduate Students:

During this project, two or three PhD graduate students were supported each year. The following students have either received their PhD in Physics, or will in the near future.

1. Nelson Garces (PhD, December 2000)
2. Madalina Chirila, (PhD, December 2003)
3. Wei Hong, (PhD, December 2003)

Publications Citing Support from this Project:

1. "Identification of a Pb-Related Ti^{3+} Center in Flux-Grown KTiOPO_4 ," K. T. Stevens, L. E. Halliburton, M. Roth, N. Angert, and M. Tseitlin, *Journal of Applied Physics* **88**, pp. 6239-6644 (2000).
2. "Identification of Electron and Hole Traps in KH_2PO_4 Crystals," N. Y. Garces, K. T. Stevens, L. E. Halliburton, S. G. Demos, H. B. Radousky, and N. P. Zaitseva, *Journal of Applied Physics* **89**, pp. 47-52 (2001).
3. "Production of Nitrogen Acceptors in ZnO by Thermal Annealing," N. Y. Garces, N. C. Giles, L. E. Halliburton, G. Cantwell, D. B. Eason, D. C. Reynolds, and D. C. Look, *Applied Physics Letters* **80**, pp. 1334-1336 (2002).
4. "Role of Copper in the Green Luminescence from ZnO Crystals," N. Y. Garces, L. Wang, L. Bai, N. C. Giles, L. E. Halliburton, and G. Cantwell, *Applied Physics Letters* **81**, pp. 622-624 (2002).

5. "Electron Paramagnetic Resonance and Electron-Nuclear Double Resonance Study of Ti^{3+} Centres in KTiOPO_4 ," S. D. Setzler, K. T. Stevens, N. C. Fernelius, M. P. Scripsick, G. J. Edwards, and L. E. Halliburton, *Journal of Physics: Condensed Matter* **15**, pp. 3969-3984 (2003).
6. "Electron Paramagnetic Resonance and Electron-Nuclear Double Resonance Study of Trapped-Hole Centers in LiB_3O_5 Crystals," Wei Hong, M. M. Chirila, N. Y. Garces, L. E. Halliburton, D. Lupenski, and P. Villeval, *Physical Review B* **68**, 094111/1-9 (2003).
7. "Electron Paramagnetic Resonance Study of Electron and Hole Traps in $\beta\text{-BaB}_2\text{O}_4$ Crystals," Wei Hong, L. E. Halliburton, K. T. Stevens, D. Perlov, G. C. Catella, R. K. Route, and R. S. Feigelson, *Journal of Applied Physics* **94**, pp. 2510-2515 (2003).
8. "Electron Paramagnetic Resonance Study of Ag^0 Atoms and Ag^{2+} Ions in $\beta\text{-BaB}_2\text{O}_4$ Nonlinear Optical Crystals," Wei Hong, D. Perlov, and L. E. Halliburton, *Journal of Physics D: Applied Physics* **36**, pp. 2605-2611 (2003).
9. "Identification of Point Defects Responsible for Laser-Induced Ultraviolet Absorption in LiB_3O_5 (LBO) Crystals," Wei Hong, N. Y. Garces, M. M. Chirila, and L. E. Halliburton, *SPIE Proceedings*, Vol. 4932, pp. 309-318 (2003).
10. "Observation of Paramagnetic Point Defects in BBO ($\beta\text{-BaB}_2\text{O}_4$) Crystals," Wei Hong, L. E. Halliburton, D. Perlov, K. T. Stevens, R. K. Route, and R. S. Feigelson, submitted to *Optical Materials* in August of 2003.

Presentations Citing Support from this Project:

1. "Gray Tracks and Photochromic Damage in KTP Crystals," L. E. Halliburton, K. T. Stevens, N. Y. Garces, and M. P. Scripsick, 12th American Conference on Crystal Growth and Epitaxy, Vail, CO, August 17, 2000.
2. "Identification of Point Defects in Lithium Triborate (LBO)," Wei Hong, N. Y. Garces, and L. E. Halliburton, 13th American Conference on Crystal Growth and Epitaxy, Burlington, VT, August 15, 2001.
3. "Identification of Point Defects Responsible for Laser-Induced Ultraviolet Absorption in LiB_3O_5 (LBO) Crystals," Wei Hong, L. E. Halliburton and N. Y. Garces, XXXIV Annual Symposium on Optical Materials for High Power Lasers (Boulder Damage Symposium), Boulder, CO, September 17, 2002.
4. "Characterization of Electron and Hole Traps in $\beta\text{-BaB}_2\text{O}_4$ (BBO) Crystals," Wei Hong, L. E. Halliburton, K. T. Stevens, D. Perlov, G. C. Catella, R. K. Route, and R. S. Feigelson, Third

III. Highlights of Research Results

The following paragraphs are brief summaries of the research results obtained during this three-year project. Reference is made in each case to the relevant publication.

A. Minimizing Laser-Induced Gray Tracks in KTP Crystals

[Journal of Applied Physics 88, 6239 (2000)] Electron paramagnetic resonance (EPR) and electron-nuclear double resonance (ENDOR) have been used to identify a new Ti^{3+} center in KTiOPO_4 crystals containing lead impurities. Many of the K^+ vacancies in this set of KTP crystals are compensated nonlocally by Pb^{2+} ions substituting for K^+ ions. During exposure to ionizing radiation (either 60-kV x-rays or 355-nm photons from a tripled Nd:YAG laser), "free" electrons are trapped on Ti^{4+} ions near isolated Pb^{2+} ions, thus forming the perturbed Ti^{3+} ions observed with EPR and ENDOR. Four distinct Pb-related Ti^{3+} centers are formed by a 77-K irradiation, but only one remains after a 5-min anneal at 180 K. This latter defect, labeled the $[\text{Ti}^{3+}\text{-Pb}^{2+}]_A$ center, is thermally unstable above 250 K. Angular dependence data were used to determine the g matrix, one ^{207}Pb hyperfine matrix, and two ^{31}P hyperfine matrices for the $[\text{Ti}^{3+}\text{-Pb}^{2+}]_A$ center. More generally, we note that oxygen-vacancy-associated Ti^{3+} centers could not be formed in these Pb-containing KTP crystals. Replacing oxygen-vacancy-associated Ti^{3+} centers with the less stable $[\text{Ti}^{3+}\text{-Pb}^{2+}]$ centers is expected to increase the gray-track resistance of KTP crystals used to generate the second harmonic of high power, near-infrared lasers.

When a KTP crystal containing an optimum amount of Pb is subjected to an intense laser beam in a second-harmonic-generation application, the various $[\text{Ti}^{3+}\text{-Pb}^{2+}]$ centers will form instead of oxygen-vacancy-related Ti^{3+} centers. This should significantly improve the performance of these devices because the thermal stability of the Pb-associated Ti^{3+} centers is considerably less than the thermal stability of the oxygen-vacancy-related Ti^{3+} centers. When operating a device at room temperature, either in a cw mode or at intermediate powers in a pulsed mode, the Pb-related Ti^{3+} centers will decay at a much faster rate than the replaced oxygen-vacancy-related Ti^{3+} centers, and the broad unwanted optical absorption band peaking near 550 to 600 nm, which is caused by the Ti^{3+} centers, will not build up as quickly to a level sufficient to affect device performance.

A cautionary note relates to the use of KTP in high-power, high repetition-rate laser applications. Operating under these extreme conditions at room temperature will cause the transient formation of large concentrations of Ti^{3+} centers along with their unwanted optical

absorption bands. In Pb-containing KTP crystals, the $[\text{Ti}^{3+}\text{-Pb}^{2+}]_{\text{A}}$ and related centers will appear during each laser pulse and, if they do not decay before the next pulse, will accumulate until after a few pulses there is sufficient local heating of the crystal along the beam path to allow a gray track to form. Although Pb-containing crystals may perform better in these extreme applications because of the shorter lifetime of the induced Ti^{3+} centers, they will clearly not be totally impervious to the formation of gray tracks. As an alternative way to improve the performance of KTP crystals used to frequency double high-power, high-repetition-rate lasers, we suggest that the concentration of potassium vacancies formed in the crystal during growth must be reduced.

B. Identification of Electron and Hole Traps in KDP Crystals

[Journal of Applied Physics 89, 47 (2001)] Electron paramagnetic resonance (EPR) has been used to characterize a hole trap and several electron traps in single crystals of potassium dihydrogen phosphate (KH_2PO_4 or KDP). The paramagnetic charge states of these centers are produced by ionizing radiation (e.g., x rays or a 266 nm beam from a pulsed Nd:YAG laser) and are stable for days and even weeks at room temperature. One center consists of a hole trapped on an oxygen ion adjacent to a silicon impurity located on a phosphorus site. This defect has a small, but easily observed, hyperfine interaction with the adjacent substitutional proton. The other centers are formed when an electron is trapped at an oxygen vacancy. These latter defects are best described as $(\text{PO}_3)^{2-}$ molecular ions, where the primary phosphorus nucleus is responsible for a large hyperfine splitting (500–800 G in magnitude). Five EPR spectra representing variations of these oxygen vacancy centers are observed, with the differences being attributed to the relative position of a nearby cation vacancy, either a missing proton or potassium. An angular study of the EPR spectra, conducted at room temperature, provided principal values and principal directions for the g matrices and hyperfine matrices for the hole center and two of the electron centers. Because of their greater thermal stability (compared to previously identified hole and electron traps in KDP which are only stable below 200 K), these new centers are expected to adversely affect the performance of this material when it is used to generate the third and fourth harmonics of Nd-based lasers.

C. Production of Nitrogen Acceptors in ZnO

[Applied Physics Letters 80, 1334 (2002)] At the present time, zinc oxide is receiving considerable attention because of its potential application as an ultraviolet light emitter. One of the major obstacles in the development of this material, however, is the difficulty encountered in finding an efficient p-type dopant. Most of today's ZnO crystals contain significant concentrations of shallow donors and, thus, are n-type. Known acceptors in ZnO include

lithium, copper, and zinc vacancies, but all of these are deep acceptors and do not contribute significantly to hole conduction. Recently, thin-film growers have focused on nitrogen as a shallower acceptor in ZnO. They have demonstrated that nitrogen will enter the films if N_2O or NH_3 , depending on the growth technique, is used as a source. With these successes, it is important to better understand the properties and behavior of nitrogen in ZnO, including charge states and ionization energies.

In this portion of our project, we found that nitrogen acceptors are formed when undoped single crystals of zinc oxide (ZnO) grown by the chemical vapor transport method are annealed in air or nitrogen atmospheres at temperatures between 600 and 900°C. After an anneal, an induced near-edge absorption band causes the crystals to appear yellow. Also, the concentration of neutral shallow donors, as monitored by electron paramagnetic resonance (EPR), is significantly reduced. A photoinduced EPR signal due to neutral nitrogen acceptors is observed when the annealed crystals are exposed to laser light (e.g., 364, 442, 458, or 514 nm) at low temperature. The nitrogens are initially in the nonparamagnetic singly ionized state (N^-) in an annealed crystal, because of the large number of shallow donors, and the light converts a portion of them to the paramagnetic neutral acceptor state (N^0).

D. Role of Copper in the Green Luminescence from ZnO

[Applied Physics Letters 81, 622 (2002)] Electron paramagnetic resonance (EPR), photoluminescence, and infrared optical absorption have been used to investigate a ZnO crystal before and after a thermal anneal for one hour in air at 900°C. The sample was an undoped high quality crystal grown by the chemical vapor transport method. In addition to shallow donor impurities, the crystal contained trace amounts of copper ions. Prior to the thermal anneal, these ions were all in the Cu^+ ($3d^{10}$) state and the observed luminescence at 5 K, produced by 364-nm light, consisted of a broad structureless band peaking at 500 nm. After the high-temperature anneal, the Cu^{2+} ($3d^9$) EPR spectrum was observed and the luminescence had changed significantly. The emission then peaked near 510 nm and showed structure identical to that reported by Dingle [Phys. Rev. Lett. 23, 579 (1969)]. Our data reaffirms that the structured green emission in ZnO is associated with Cu^{2+} ions.

Our results strongly suggest that Cu^+ ions are present in our as-grown (i.e., unannealed) ZnO sample. These ions are singly ionized acceptors (i.e., A^- centers). This means that a portion of the shallow donors must be singly ionized (i.e., D^+ centers) in the unannealed sample. With both A^- and D^+ centers present in the unannealed sample, we have the classic situation to observe donor-acceptor pair (DAP) recombination if the sample is pumped with either an above-band-gap or near-band-gap laser. For these reasons, we suggest that the unstructured emission

peaking near 500 nm in ZnO is due to DAP recombination involving shallow donors and copper acceptors. We note that DAP recombination involving copper acceptors is common in other II-VI materials. The assignment of the unstructured emission band to DAP recombination requires a neutral acceptor level approximately 0.5 eV above the top of the valence band and a strong electron-phonon coupling. In general, because ZnO has a more ionic nature and relatively deeper levels for donors and acceptors, emission bands from this material may not simply reflect traditional semiconductor behavior, i.e., shifts in DAP emission may not be as large when the excitation power and the temperature are varied. This is primarily because the donor energy level is fairly deep (i.e., 60 meV), corresponding to a Bohr radius of 16.7 Å.

E. EPR and ENDOR from Ti^{3+} Centers in KTP Crystals

[Journal of Physics: Condensed Matter **15**, 3969 (2003)] Electron paramagnetic resonance (EPR) and electron-nuclear double resonance (ENDOR) have been used to characterize four Ti^{3+} centers in undoped crystals of potassium titanyl phosphate (KTiOPO_4 or KTP). These $3d^1$ defects ($S = 1/2$) are produced by ionizing radiation (either 60-kV x-rays or 355-nm photons from a tripled Nd:YAG laser), and form when the regular Ti^{4+} ions in the crystal trap an electron. Two of these trapped-electron centers are only observed in hydrothermally grown KTP and the other two are dominant in flux-grown KTP. Both of the Ti^{3+} centers in hydrothermally grown crystals have a neighboring proton (i.e., an OH^- molecule). In the flux-grown crystals, one of the Ti^{3+} centers is adjacent to an oxygen vacancy and the other center is tentatively attributed to a self-trapped electron (i.e., a Ti^{3+} center with no stabilizing entity nearby). The g matrix and phosphorus hyperfine matrices are determined for all four Ti^{3+} centers, and the proton hyperfine matrix is determined for the two centers associated with OH^- ions. These Ti^{3+} centers contribute to the formation of the gray tracks often observed in KTP crystals used to generate the second harmonic of high power, near-infrared lasers.

The two centers present in hydrothermally grown material are labeled Centers I_{hyd} and II_{hyd} and the two centers present in flux-grown material are Centers I_{flx} and A_{flx} . Centers I_{hyd} and II_{hyd} have the Ti^{3+} ion occupying the inequivalent Ti(1) and Ti(2) crystal sites, respectively, and they each have a proton bonded to an adjacent oxygen (OT) ion. These protons, in the form of OH^- ions, provide the stabilizing influence to hold the unpaired electron at the titanium site. Center A_{flx} is a Ti^{3+} ion located adjacent to an oxygen vacancy (i.e., a missing OT ion) and is the most stable of the four centers investigated.

Identification of the stabilizing mechanism for each of the different Ti^{3+} centers formed in undoped KTP helps to explain why gray tracks form in some crystals and not in others. It is now well established that significant concentrations of potassium vacancies are present in all

KTP crystals (both hydrothermally grown and flux-grown). These K^+ vacancies are charge compensated, in large part, by OH^- molecular ions in the hydrothermally grown crystals and by oxygen vacancies in the flux-grown crystals. During exposure to x-rays or an intense laser beam, these same entities (the OH^- ions or oxygen vacancies) act as stabilizers for the Ti^{3+} centers. The thermal stability of each Ti^{3+} center depends on the nature of its specific stabilizing entity (e.g., Centers I_{hyd} and II_{hyd} in hydrothermally grown KTP are considerably less stable than Center A_{flux} in flux-grown KTP). In general, crystals in which larger concentrations of the more stable Ti^{3+} centers can be produced may be expected to have a greater susceptibility to gray tracking. Equally important, the nature and concentration of hole traps (impurities such as silicon, platinum, iron, chromium, etc.) in a particular KTP crystal may significantly affect its resistance to bulk optical damage.

F. EPR and ENDOR Study of Trapped Hole Centers in LBO

[Physical Review B 68, 094111 (2003)] Electron paramagnetic resonance (EPR) and electron-nuclear double resonance (ENDOR) have been used to characterize two distinct hole centers in single crystals of LiB_3O_5 (commonly referred to as LBO). Irradiating a crystal at 77 K with x rays produces an intense four-line holelike EPR signal, with the structure arising from the hyperfine interaction with one ^{11}B nucleus. Warming the crystal to approximately 130 K destroys the first hole center and allows a second less intense four-line holelike EPR signal to be observed (also interacting with one ^{11}B nucleus). The second hole center decays between 150 and 200 K. EPR and ENDOR angular dependence data were used to determine the g matrix and the ^{11}B hyperfine and nuclear quadrupole matrices for each hole center. We suggest that the first (less thermally stable) center is a self-trapped hole. In this defect, the hole is localized primarily on an oxygen ion between a threefold bonded boron and a fourfold bonded boron, and the self-trapping occurs because of a significant relaxation of the neighboring fourfold boron away from the hole. Gaussian 98 calculations, using a $(B_3O_7H_4)^0$ cluster to represent the defect and the nearby lattice, support this self-trapping mechanism. A similar model is suggested for the second hole center, except in this case a neighboring lithium vacancy is included to provide the increased thermal stability.

A major goal of our present study was to understand the point defects that participate in the transient optical absorptions produced in LiB_3O_5 when these crystals are used in room-temperature frequency conversion applications involving ultraviolet beams from high-power pulsed lasers. The trapped-hole centers we have discovered are of definite interest in this regard. Our self-trapping model for the dominant low-temperature hole center suggests that this defect will be formed in every LiB_3O_5 crystal and, because of its intrinsic nature, cannot be eliminated simply by improvements in crystal growth. However, the "steady-state" concentration of self-

trapped holes formed during operation of ultraviolet devices should be considerably decreased if efforts are made to reduce the number of oxygen vacancies that serve as the corresponding primary electron trap in this lattice. Without a long-lived electron trap, the self-trapped holes will have very short lifetimes and significant concentrations cannot build up on millisecond time scales. Thus, we suggest that modifications in the crystal growth process designed to minimize the number of oxygen vacancies may help to alleviate problems arising from transient ultraviolet absorption bands in nonlinear optical devices utilizing LiB_3O_5 .

G. EPR Study of Electron and Hole Traps in BBO Crystals

[Journal of Applied Physics 94, 2510 (2003)] Electron paramagnetic resonance (EPR) has been used to investigate point defects in single crystals of $\beta\text{-BaB}_2\text{O}_4$ (commonly referred to as BBO). An irradiation with x rays at 77 K produces two dominant EPR spectra, one electronlike and the other holelike. The trapped-electron center exhibits a 16-line hyperfine pattern from two boron nuclei. With the magnetic field parallel to the c axis, its g value is 1.9993 and the ^{11}B hyperfine splittings are 49 and 42 G. We suggest that this defect is an oxygen vacancy with a trapped electron nearly equally shared by the two neighboring boron ions. In contrast, the trapped-hole center exhibits a four-line hyperfine pattern due to one boron, and is assigned to a hole localized on a nonbridging oxygen ion with no other defects nearby (i.e., a self-trapped hole). With the magnetic field along the c axis, this center has a g value of 2.0113 and a ^{11}B hyperfine splitting of 14.1 G. Warming the crystal to temperatures between 80 and 90 K destroys the initial four-line hole spectrum and introduces other hole centers (most likely perturbed by nearby Na^+ ions substituting for Ba^{2+} ions or by barium vacancies).

A primary application of BBO crystals is frequency conversion in the visible and near ultraviolet. The defects discovered in our present investigation will form during many of these applications (e.g., via two-photon absorption) and will result in transient absorption bands that may degrade the performance of the nonlinear optical devices. This suggests that it may be possible to produce improved BBO crystals for high-power laser applications in the ultraviolet by making modifications in the growth process that reduce the number of oxygen vacancies, substitutional Na^+ ions, and Ba^{2+} vacancies. Because of charge compensation, it is sufficient to implement growth strategies that either minimize the oxygen vacancies or the substitutional Na^+ ions and Ba^{2+} vacancies.

H. Diffusion of Silver into BBO Crystals

[Journal of Physics D: Applied Physics 36, 2605 (2003)] Silver ions have been diffused into single crystals of $\beta\text{-BaB}_2\text{O}_4$ (commonly referred to as BBO). The crystals were wrapped in

silver foil and then held in air at 760°C for periods of time ranging from 1 to 7 h. This treatment resulted in Ag^+ ions occupying both Ba^{2+} sites and interstitial sites within the crystal. After the diffusion, the crystal was irradiated at room temperature with 60-kV x rays. Three distinct paramagnetic defects, one holelike and two electronlike, were produced by the x rays, and observed with electron paramagnetic resonance (EPR) at temperatures between 15 and 80 K. The Ag^+ ions substituting for Ba^{2+} ions trapped radiation-induced holes and became paramagnetic Ag^{2+} ions. At the same time, interstitial Ag^+ ions trapped electrons and became paramagnetic Ag^0 atoms. There are two distinct versions of these latter centers. The EPR spectra of the Ag^0 atoms show resolved hyperfine from the $^{107,109}\text{Ag}$ isotopes, as well as from a neighboring $I = 3/2$ nucleus (possibly a Na^+ impurity substituting for a Ba^{2+} ion). All of the radiation-induced EPR signals were stable at room temperature for hours.

We suggest that the silver ions enter the BBO lattice through an ion-exchange process. For every two Ag^+ ions entering the crystal, one Ba^{2+} ion leaves. One of these entering Ag^+ ions will remain as an interstitial in the crystal and the other will “fall” into the barium vacancy that is created by the exiting barium ion. Thus, a diffusion treatment results in approximately half of the Ag^+ ions occupying interstitial sites and the other half occupying barium sites. Previous work has suggested that barium vacancies are present in as-grown BBO crystals, and we anticipate that these cation vacancies may enhance the diffusion of the Ag^+ ions into the lattice during the early treatments. With longer treatments, the concentration of substitutional Ag^+ ions in the crystal is expected to exceed the as-grown concentration of barium vacancies, and the enhancement effect will become less important.

I. Origin of Ultraviolet Absorption in LBO Crystals

[SPIE Proceedings, Vol. 4932, 309 (2003)] The electron paramagnetic resonance (EPR) technique has been used to investigate point defects in single crystals of BBO ($\beta\text{-BaB}_2\text{O}_4$). This borate compound is a widely used nonlinear optical material, especially in the ultraviolet region, and point defects are expected to play a role in its device performance. There were no observable EPR spectra in our as-grown BBO crystals. However, an irradiation at room temperature with x rays produced two stable EPR signals. One of these spectra, containing ten hyperfine lines when the magnetic field is parallel to the crystal's c axis, is assigned to a hole trapped on an oxygen ion adjacent to a barium vacancy. The ten lines are due to interactions with the two neighboring ^{11}B nuclei. The other radiation-induced spectrum consists of a single line with an effective g value of 2.017 when the magnetic field is along the c axis. We tentatively assign this spectrum to Ni^+ ions substituting for Ba^{2+} ions. In separate experiments, it was found that heating an as-grown BBO crystal to 760°C for several hours produced an EPR spectrum due to Cu^{2+} ions. Subsequent exposure at room temperature to x rays reduces the

intensity of the Cu^{2+} spectrum.

J. Room-Temperature-Stable Point Defects in BBO Crystals

[Submitted to Optical Materials] The electron paramagnetic resonance (EPR) technique has been used to investigate point defects in single crystals of BBO ($\beta\text{-BaB}_2\text{O}_4$). This borate compound is a widely used nonlinear optical material, especially in the ultraviolet region, and point defects are expected to play a role in its device performance. There were no observable EPR spectra in our as-grown BBO crystals. However, an irradiation at room temperature with x rays produced two stable EPR signals. One of these spectra, containing ten hyperfine lines when the magnetic field is parallel to the crystal's c axis, is assigned to a hole trapped on an oxygen ion adjacent to a barium vacancy. The ten lines are due to interactions with the two neighboring ^{11}B nuclei. The other radiation-induced spectrum consists of a single line with an effective g value of 2.017 when the magnetic field is along the c axis. We tentatively assign this spectrum to Ni^{+} ions substituting for Ba^{2+} ions. In separate experiments, it was found that heating an as-grown BBO crystal to 760°C for several hours produced an EPR spectrum due to Cu^{2+} ions. Subsequent exposure at room temperature to x rays reduces the intensity of the Cu^{2+} spectrum.